Diffusion of Ferric and Ferrous Iron in Silicate Melts

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Beamline: **X26A**

Introduction: Understanding the behaviour of iron in silicate melts at different oxygen fugacities is crucial to the understanding of igneous petrogenesis. Because of the differing charges of ferric and ferrous iron they can potentially diffuse through melts at significantly different rates. The differing rates of diffusion can act as a fractionation mechanism of ferric and ferrous iron during crystal growth, crystal dissolution, the separation of a fluid phase from the melt, and the mixing of two melts. This fractionation can ultimately affect the stability and distribution of minerals during crystallization of the magma. In particular, the stability of magnetite (Fe_3O_4) is critically dependent upon the concentration of Fe^{3+} in the melt. Furthermore, the results of this study can have industrial applications in the manufacture of iron-containing glasses.

Methods and Materials: Bajt et al. (1994, 1995) have demonstrated that the energy of the pre-edge peak in the X-ray absorption near-edge structure (XANES) spectra can be used to accurately determine the ferric/ferrous ratio in silicate crystals and glasses (quenched melts). XANES spectra of a series of experiments designed to investigate the dissolution of iron metal into a synthetic silicate melt of the composition of the diopside-anorthite eutectic were measured. In these experiments an alumina capsule contained a ~1 mm^3 cube of iron metal surrounded by the melt. The iron was allowed to dissolve for times varying from 20 minutes to 16 hours at temperatures between 1300°C and 1500°C and then the sample was quenched, mounted in epoxy and ground open to reveal the cube and the glass surrounding it. Typical experiments displayed little evidence for significant iron dissolution of the cube: all corners were still at approximately right angles. Electron microprobe analysis of total iron as FeO* demonstrated that diffusion had occurred at distances up to 1000's of μm away from the cube-melt interface.

XANES spectroscopy of these samples was performed on beamline X26A with a beam size of approximately 10 μm diameter. Analytical traverses away from the cube-melt interface were made with 50 μm steps near the cube and 100 μm at distances greater than 500 μm from the interface. Calibration of the ferric/ferrous ratio was performed using the energy of the pre-edge peak for the mineral standards fayalite (Fe_2SiO_4) with only Fe^{2+} and magnetite with both Fe^{2+} and Fe^{3+}. The ferric/ferrous ratio at each point was combined with the total iron at that point measured by electron microprobe to calculate the concentrations of FeO and Fe_2O_3 in the melt. The measured profiles of FeO and Fe_2O_3 were used to calculate the diffusion of Fe^{2+} and Fe^{3+} in the melt assuming a source of constant geometry and fixed location in space, both of which are good assumptions for the experiments of this study. However, discussions with J.S. Delaney (Rutgers U.) after the XANES analyses were finished revealed that the standards used may not give reliable results for glasses. Thus, we are currently characterizing the oxidization states in homogeneous glasses analyzed by XANES for FeO and Fe_2O_3 by Mossbauer spectroscopy to ascertain the accuracy of our preliminary analyses.

Results: Because of the calibration problems only three experiments at 1315°C have been analyzed and used for the measurement of ferric and ferrous iron diffusion coefficients (e.g. Fig. 1). The diffusion profiles demonstrate that as expected ferrous iron diffuses more rapidly than ferric iron. At 1315°C in air the diffusion coefficient for Fe^{2+} in this system is 7.2×10^{-12} m^2 s^{-1} and for Fe^{3+} is 2.5×10^{-12} m^{2}s^{-1}. At an oxygen fugacity equivalent to the wüsite-magnetite oxygen fugacity ($\log f_{O2} = -7.5$) the diffusion coefficient of ferrous iron is 9.8×10^{-13} m^{2}s^{-1}; unfortunately the diffusion coefficient for ferric iron could not be measured in this experiment because no profile was discernable.

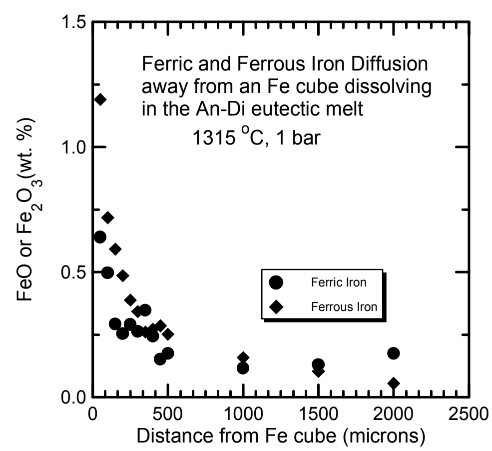

Figure 1. Diffusion profiles for Fe^{2+} and Fe^{3+}

Conclusions: Measurements of Fe^{3+} and Fe^{2+} diffusion in a silicate melt at 1315°C support the hypothesis that oxidation state exerts a significant effect on the diffusion of a cation. These preliminary results demonstrate clearly that ferric and ferrous iron diffuse at different rates in the silicate melt investigated and that oxygen fugacity exerts a significant effect on the diffusion of both iron species. The difference in diffusion coefficients at the temperature studied is significant enough to potentially create fractionation between ferric and ferrous iron by diffusive processes in natural magmatic systems.

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